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SYNERGISTIC COMPOSITION FOR REGULATING PLANT GROWTH

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(56) Prior Art Documents
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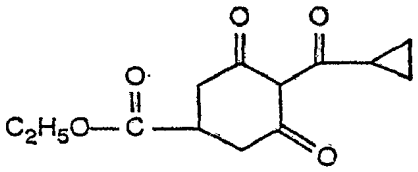
(57) Claim

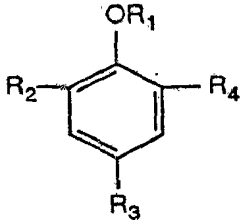
1. A synergistically acting composition for regulating plant growth, which is characterized that it contains besides inert carriers, auxiliaries and adjuvants, as active component 4-cyclopropionyl-3,5-cyclohexanedione-1-carboxylic acid of formula I



(I)

besides a synergistically active amount of a further active compound selected from among

a) phenolethers of the formula II



(II)

wherein

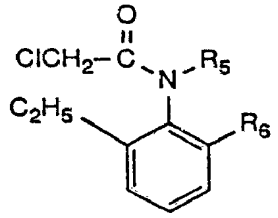
R_1 is an acid or the C_1-C_4alkyl ester of a radical -CH_2COOH, -$CH(CH_3)COOH$, -$(CH_2)_3COOH$ or the nitrobenzoic-5-yl radical,

R_2 is chlorine or methyl,

. . ./2

R_3 is chlorine and
R_4 is hydrogen, chlorine or methyl; or

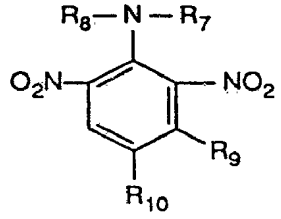
b) chloracetanilides of the formula III



(III)

wherein
R_5 is methyl or ethyl and
R_6 is methoxymethyl, ethoxymethyl or 2-methoxy-1-methylethyl; or

c) dinitroanilines of the formula IV



(IV)

wherein
R_7 is hydrogen or C_1-C_4alkyl,
R_8 is C_1-C_4alkyl, benzyl or halobenzyl,
R_9 is hydrogen or halogen and
R_{10} is methyl, trihalomethyl or chlorine; or

d) N-benzoyl-N-(3,4-dichlorophenyl)-DL-alanine acid ethyl ester; or

e) a quaternary ammonium salt selected from among 1,1-dimethylpiperidine chloride and 2-chloro-N,N,N-trimethylethylammonium chloride; or

f) 2-chloroethylphosphonic acid; or

g) 1-phenyl-4,4-dimethyl-2(1H-1,2,4-triazol-1-yl)-pent-1-en-3 -ol; or

h) 5-(1-methylthioxycyclopropane-1-yl)-2-(trans-3-chloroallylo ximino)-propionyl-cyclohexane-1,3-dione.

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COMPLETE SPECIFICATION

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Complete Specification for the invention entitled:

Synergistic Composition for Regulating Plant Growth

The following statement is a full description of this invention, including the best method of performing it known to me/us

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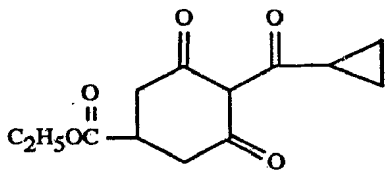
PS/5-17876/=

Synergistic Composition for Regulating Plant Growth

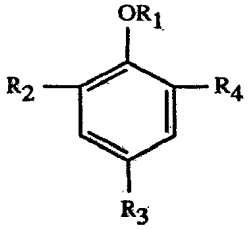
Abstract of the Disclosure

The inventions relates to a synergistically acting compotistion and to a method for regulating plant growth, which contains as active compound of formula I, the ethylester of 4-cyclopropyl-3,5-cyclohexanedione-1-carbonic acid of the formula I



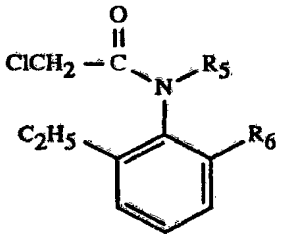
(I)

together with a synergistically active amount of a phenolether of the formula II



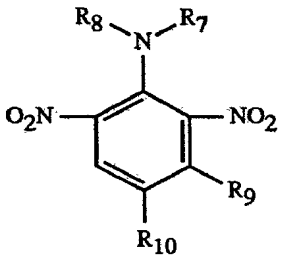
(II), or

a chloroacetanilide of the formula III



(III), or

a dinitroaniline of the formula IV



(IV), or

the ethylester of N-benzoyl-N-(3,4-dichlorophenyl)-DL-alanine, or of 1,1-dimethyl-pyridine-chloride, 2-chloroethyl-N,N-trimethylammonium chloride, 2-chlorethyl-phosphonic acid, 1-phenyl-4,4-dimethyl-2-(1H-1,2,4-triazole-1-yl)-pent-1-en-3-ol, 1-(4-chlorophenyl)-3,3-dimethyl-1-(1H-1,2,4-triazole-1-yl)-butan-2-ol or of 5-(1-methyl-thiocyclopropan-1-yl)-[(trans-2-chlorallyloximino)-propionyl]-cyclohexane-1, 3-dione.

In the formulae II to IV, R_1 to R_{10} have the meaning given in the description. The composition serves to regulate plant growth, especially inhibiting the growth of cereal and grass and is used preferably in post-emergent application.

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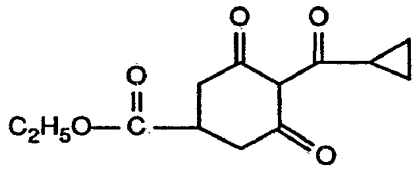
Synergistic Composition for Regulating Plant Growth

The present invention relates to synergistic compositions containing plant growth regulating combinations of active compounds. The compositions according to this invention are suitable for regulating, especially inhibiting the growth of cultures of crop plants.

The invention relates further to a method for regulating, especially inhibiting the growth of crop plants, especially of cereal, grass and other cultures and to the use of the new compositions.

Form the European Patent No. 126,713 respectively the US Patent No. 4,693,475 the ethyl ester of 4-cyclopropionyl-3,5-cyclohexanedione-1-carboxylic acid of formula



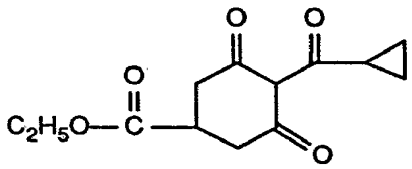
(I)

has been known. This active compound has good plant growth regulating, especially plant growth inhibiting properties.

Surprisingly the plant growth regulating property of this compound can be enhanced in a synergistic manner, by adding to it certain active compounds chosen from the group consisting of

a) phenol ether,
b) chloroacetanilide,
c) dinitroaniline
d) the ethyl ester of N-benzoyl-N-(3,4-diphenyl)-DL-alanine,
e) quaternary ammonium salts
f) 2-chloroethylphosphonic acid
g) triazole derivatives and
h) 5-(1-methylthiocycloprop-1-yl)-2-[1-(trans-3-chlorallyloximino)-propionyl]-cyclohexane-1,3-dione.

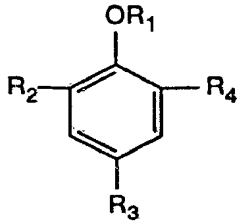
Object of the invention are therefore synergistic compositions for regulating plant growth, which contain, besides inert carriers, auxiliaries and adjuvants, as active compound 4-cyclopropionyl-3,5-cyclohexanedione-1-carboxylic-acid ethyl ester of the formula I



(I)

and additionally a synergistically active amount of another active compound selected from among

a) phenol ethers of the formula II



(II)

wherein

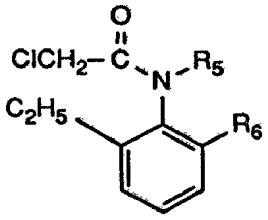
R_1 is an acid or the C_1-C_4alkyl ester of a radical $-CH_2COOH$, $-CH(CH_3)COOH$, $-(CH_2)_3COOH$ or the nitrobenzoic-5-yl radical,

R_2 is chlorine or methyl,

R_3 is chlorine and

R_4 is hydrogen, chlorine or methyl; or

b) chloracetanilides of formula III



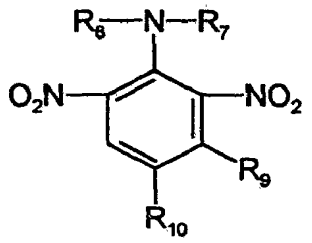
(III)

wherein

R_5 is methyl or ethyl and

R_6 is methoxymethyl or 2-methoxy-1-methylethyl; or

c) dinitroanilines of the formula IV



(IV)

wherein

R_7 is hydrogen or C_1-C_4alkyl,

R_8 is C_1-C_4alkyl, benzyl or halobenzyl,

R_9 is hydrogen, methyl or halogen and

R_{10} is methyl, trihalomethyl or chlorine; or

d) N-benzoyl-N-(3,4-dichlorophenyl)-DL-alanine acid ethyl ester (V); or

e) a quaternary ammonium salt selected from among 1,1-dimethylpiperidine chloride (VIa) and 2-chloro-N,N,N-trimethylethylammonium chloride (VIb);or

f) 2-chloroethylphosphonic acid (VII); or

g) 1-phenyl-4,4-dimethyl-2(1H-1,2,4-triazol-1-yl)-pent-1-en-3-ol (VIII); or

h) 5-(1-methylthioxycyclopropan-1-yl)-2-(trans-3-chloroallyloximino)-propionyl-cyclohexane-1,3-dione (IX).

The invention also relates to the use of the plant growth regulating compositions, which contain an active compound of the formula I, together with a synergistically acting amount of a compound of the formulae II to IX, e.g. for inhibiting the growth of plants.

Accordingly, there is also provided according to the invention a method of regulating plant growth, which is characterized in that one applies to the plants or their locus an active amount of the composition of the invention, respectively a tank mix containing the active compound of the formula I and a mixing partner of formulae II to IX.

There is further provided according to the invention a method of inhibiting plant growth in field cultures of useful plants and grasses which is characterized in that one applies to the plants post-emergently an active amount of a composition according to the invention.

The compounds of the formulae I to IX are known.

Ethyl-4-cyclopropyl-3,5-cyclohexanedionecarboxylate of formula I is e.g. prepared as follows:

30 ml of cyclopropanoyl chloride are added dropwise to a solution of 60g of 3,5-cyclo-

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hexanedionecarboxylate and 25 ml of pyridine in 400 ml of dichloroethane. When everything is added, the mixture is stirred for a further 15 hours at room temperature. The reaction solution is then filtered and the filtrate is washed with 1N hydrochloric acid, dried and concentrated. The O-acylated intermediary product so obtained, is taken up in 200 ml of dichloroethane, 4 g of 4-dimethylaminopyridine are added and the reaction mixture is refluxed for 4 hours. The cooled reaction solution is then washed with 1N hydrochloric acid, dried, concentrated, and the residue is chromatographed for purification over a small amount of silica gel. After evaporation of the solvent, one obtains the ethyl 4-cyclopropanoyl-3,5-cyclohexanedionecarboxylate as a pale oil with a refractive index of n_0^{30} 1.5350.

The following compounds of the formulae II to IX are to be mentioned:

- Phenol ethers of the formula II:

IIa) the methylester 2-nitro-5-(2,4-dichlorophenoxy)benzoic acid, common name "Bifenox", known from aus USP 3 776 715, see also The Pesticide Index 7th Ed. by R. Worthing and S.B. Walker, published by the British Crop Protection Council, Lavenham Press Ltd. 1983.

IIb) 2-(4-chloro-2-methylphenoxy)-propionic acid, common name "Mecoprop" or "MCPP", known from GBP 820 180, see also "The Pesticide Manual 7th Ed. 1983 7860".

IIc) 2-(2,4-dichlorophenoxy)acetic acid common name "2,4 D", see "The Pesticide Manual 7th Ed. 1983 3780".

IId) 2-(4-chloro-2-methylphenoxy)acetic acid, common name "MCPA", see "The Pesticide Manual 7th Ed. 1983 7790".

IIe) 4-(4-chloro-2-methylphenoxy)butyric acid common name "MCPB", see "The Pesticide Manual 7th Ed. 1983 7810".

-Chloroacetanilides of the formula III:

IIIa) 2-chloro-2'-ethyl-6'-methyl-N-(2-methoxy-1-methylethyl)-acetanilide; common name

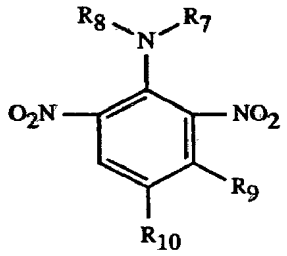
"Metolachlor"; (described in "The Pesticide Manual", 8th ed. (1987), p. 568, Ed. C.R. Worthing; The British Crop Protection Council, Thornton Heath, GB).

IIIb) 2-chloro-2',6'-diethyl-N-methoxymethyl-acetanilide; common name "Alachlor"; (described in "The Pesticide Manual", 8th ed. (1987), p. 5, Ed. C.R. Worthing; The British Crop Protection Council, Thornton Heath, GB).

IIIc) 2-chloro-N-ethoxymethyl-6'-ethyl-acet-o-toluidide; common name "Acetochlor"; (described in "The Pesticide Manual", 8th Ed. (1987) p. 2, C.R. Worthing; The British Crop Protection Council, Thornton Heath, GB).

IIId) 2-chloro-N-(methoxycarbonylaminomethyl)-2',6'-diethyl-acetanilide, common name "Amidochlor".

- 2,6-Dinitroanilines of the formula IV:



(IV)

wherein

R_7 is hydrogen or C_1-C_4alkyl,
R_8 is C_1-C_4alkyl, benzyl or halobenzyl,
R_9 is hydrogen or halogen,
R_{10} is methyl, trihalomethyl or chlorine.

Among the compounds of formula IV the following individual compounds are especially active:

IVa) N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitroaniline, common name "Pendimethalin" known from USP 4 199 669, see the "The Pesticide Manual, 7th Ed. 1983 p. 9390".

IVb) N-ethyl-N(2'-chloro-6'-fluorobenzyl)-2,6-dinitro-4-trifluoromethylaniline, common name "Flumetralin" known from USP 4 169 721, see "The Pesticide Manual, 7th Ed.

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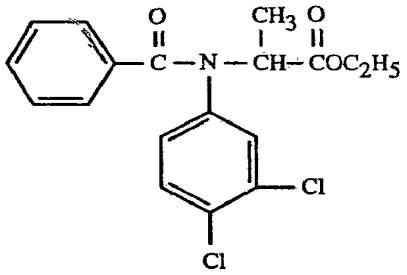
1983 p. 6480".

IVc) N_1,N_1-diethyl-2,6-dinitro-4-trifluormethyl-1,3-phenyldiamine, common name "Dinitramine", known from USP 3 617 252, see "The Pesticide Manual 7th Ed. 1983 5070.

- The ethylester of N-benzoyl-N-(3,4-dichlorophenyl)-DL alanine of the formula V

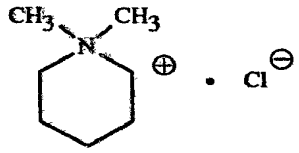


(V)

common name "Benzoylprop-ethyl", known from the GBP 1 164 160, see "The Pesticide Manual 7th Ed. 1983 850".

- Quaternary ammonium salts of the formula VI:

VIa) The chloride of 1,1-dimethylpiperidine



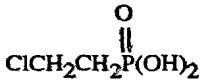
common name "Mequipat", known from DE-A 2 207 575, see "The Pesticide Manual 7th Ed. 1983 7920.

VIb) The chloride of 2-chloroethyl-N,N,N-trimethylammonium

$$ClCH_2CH_2N(CH_3)_3^{\oplus} \cdot Cl$$

common name "Chlomequat", known from GBP 944 807, see "The Pesticide Manual 7th Ed. 1983 5680".

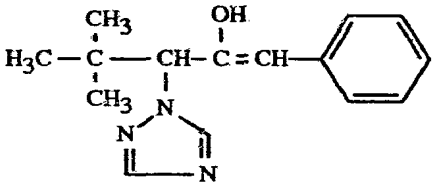
- 2-Chloroethylphosphonic acid of the formula VII:



(VII)

common name "Ethephon", known from USP 3 879 188, see "The Pesticide Manual 7th Ed. 1983 5680".

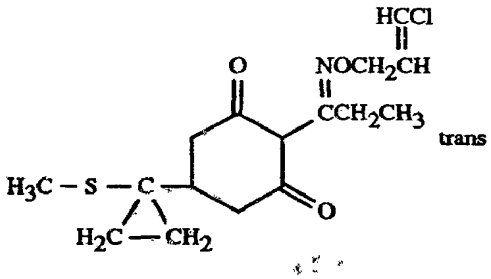
- 1-Phenyl-4,4-dimethyl-2(1H-1,2,4-triazole-1-yl)-pent-1-en-3- ol of the formula VIII



(VIII)

common name "Triapenthenol" known from "The British Crop Protection Conference" Weeds Vol. 1 p. 113-128 1985.

- 5-(1-Methylthiocyclopropan-1-yl)-2-[1-(trans-3-chloroallyloximino)-propionyl]-cyclohexane-1,3-dione of the formula IX



(IX)

known from EP-A 243 313 or USP 4,909,835.

On the other hand other compounds with herbicidal or plant growth regulating properties, that were tested, showed surprisingly no synergistic enhancement of activity at all in combination with the active compound of formula I.

Plant growth regulators are substances which cause agronomically desired biochemical and/or physiological and/or morphological alterations in/on the plant.

The active substances contained in the compositions according to the invention have various effects on the plant growth, depending on the point in time of application, the dosage, the type of application and the environmental conditions. For example, the plant growth regulating combinations of this invention can inhibit the vegetative growth of plants. This type of action is interesting on lawns, in the production of ornamental plants, in orchards, on verges, on sports grounds and industrial terrain, but also in the targeted inhibition of secondary shoots, such as in tobacco. In arable farming, inhibition of the vegetative growth in cereals by means of thickened stems results in reduced lodging, and similar agronomical effects are achieved in oil seed rape, sunflowers, maize and other crop plants. Moreover, inhibition of the vegetative growth makes it possible to increase the number of plants per unit area. Another field of application of growth inhibitors is the selective control of ground-cover plants in plantations or crops with substantial distances between the rows by powerful inhibition of growth without killing these ground-cover plants, which results in the elimination of competition with the main crop but agronomically positive effects, such as prevention of erosion, nitrogen fixation and loosening of the soil, are retained.

Plant growth regulators can stimulate crop yield in a quantitative way (e.g. flow of latex) or a qualitative way (e.g. sugar content), the apical dominance can be broken and the forming of side-shoots promoted (e.g. in ornamental plants), the drop of fruit and flowers can be promoted (e.g. thinning out in fruit trees in order to break the alternance, fruit abscission in olives, making possible mechanical harvesting), the ripening of fruits can be harmonised, sped up or delayed by means of growth regulators (e.g. opening of the capsules in cotton, ripening of tomatoes or bananas).

A method for inhibiting plant growth is taken to mean that man interferes with the natural development of the plant without altering, in the sense of a mutation, the life cycle of the plant, which is determined by the genetic make-up. The method of growth regulation is applied at a point in time of development of the plant to be determined in the individual case. The active substances of the formula I can be applied before or after emergence of the plants, for example as early as in the seed stage, or to the seedlings, to roots, tubers, stalks, leaves, flowers or other parts of the plant. This can be effected for example by applying the mixture of active substances of this invention itself or in the form of an agent

to the plants and/or by treating the culture substrate of the plant (soil).

Plants can be made more resistant to environmental stress such as draught, cold or salt content in the soil with plant growth regulators. The defoliation of culture plants can be induced at a fixed time so that mechanical harvesting of crops like cotten, potatoes or vines becomes facilitated respectively made possible.

The synergistic compositions according to this invention (crop plant growth inhibitors are preferably used for growth inhibition in monocotyledonous cultures, such as cereal, grasses but also in dicotyledonous cultures with post-emergent application.

The synergistic mixtures according to this invention are used in general in application rates of 50 g/ha to 5000 g/ha. The proportion between the amount of compound of the formula I and the synergistically active amount of the compound of formula II to IX can vary in wide ranges. As a rule the amount of compound of the formula I to the synergistically active amount of mixing partner of the formula II to IX lies between 100:1 to 1:20, preferably between 1:1 to 1:10.

The present invention includes also the preparation of agrochemical compositions, which is characterised by intimely mixing the active substances with one or several of the substances or groups of substances described herein. Included is also a method for treating plants, which is distinguished by the application of the compositions according to this invention.

Mixtures of the active compounds of the formula I and II to IX are generally used in the form of combinations and can be applied to the plants or the area to be treated simultaneously or successively.

Suitable carriers and adjuvants may be solid or liquid and correspond to appropriate substances used in the technique of formulation, such as e.g. natural or regenerated mineral material, solvents, dispergents, wetting agents, adhesifs, thickeners, binding agents or fertilizers.

The compositions according to the invention are used in the unchanged form or preferably together with adjuvants usual in formulation technique and are used therefore e.g. as emulsion concentrates or solutions which can be sprayed directly or after dilution, diluted

emulsions, meltable powders, dusts, granulates, or they are worked up e.g. by capsulation e.g. in polymeric material in the known way. According to the pursued goal and the given circumstances, applications like spraying, atomizing, dusting, scattering, spreading or powdering are selected as well as the appropriate kind of formulation. Favorable application rates are in general 10 to 5 kg of active substance (AS) per ha; preferably 100 g to 2 kg AS/ha.

The formulations, i.e. the compositions, containing the compound of formula I with a compound of the formulae II to IX and, where appropriate, a solid or liquid adjuvant, are prepared in known manner, e.g. by homogeneously mixing and/or grinding the active ingredients with extenders, e.g. solvents, solid carriers and, where appropriate, surface-active compounds (surfactants).

Suitable solvents are: aromatic hydrocarbons, preferably the fractions containing 8 to 12 carbon atoms, e.g. xylene mixtures or substituted naphthalene, phthalates such as dibutyl phthalate or dioctyl phthalate, aliphatic hydrocarbons such as cyclohexane or paraffins, alcohols and glycols and their ethers and esters, such as ethanol, ethylene glycol, ethylene glycol monomethyl or monoethyl ether, ketones such as cyclohexanone, strongly polar solvents such as N-methyl-2-pyrrolidone, dimethyl sulfoxide or dimethylformamide, as well as vegetable oils or epoxidised vegetable oils, such as epoxidised coconut oil or soybean oil; or water.

The solid carriers used e.g. for dusts and dispersible powders, are normally natural mineral fillers such as calcite, talcum, kaolin, montmorillonite or attapulgite. In order to improve the physical properties it is also possible to add highly dispersed silicic acid or highly dispersed absorbent polymers. Suitable granulated adsorptive carriers are porous types, for example pumice, broken brick, sepiolite or bentonite; and suitable nonsorbent carriers are, for example, calcite or sand. In addition, a great number of pregranulated materials of inorganic or organic nature can be used, e.g. especially dolomite or pulverised plant residues e.g. cork powder or sawdust. Especially suitable adjuvants are further phospholipides.

Suitable surface-active compounds are non-ionic, cationic and/or anionic surfactants having good emulsifiying, dispersing and wetting properties. The term "surfactants" will also be understood as comprising mixtures of surfactants.

Both so-called water-soluble soaps and also water-soluble synthetic surface-active compounds are suitable anionic surfactants.

Suitable soaps are the alkali metal salts, alkaline earth metal salts or unsubstituted or substituted ammonium salts of higher fatty acids ($C_{10}C_{22}$), e.g. the sodium or potassium salts of oleic or stearic acid or of natural fatty acid mixtures which can be obtained e.g. from coconut oil or tallow oil. Mention may also be made of fatty acid methyllaurin salts.

More frequently, however, so-called synthetic surfactants are used, especially fatty sulfonates, fatty sulfates, sulfonated benzimidazole derivatives or alkylarylsulfonates.

The fatty sulfonates of sulfates are usually in the form of alkali metal salts, alkaline earth metal salts or unsubstituted or substituted ammonium salts and contain a C_8-C_{22}alkaly radical which also includes the alkyl moiety of acyl radicals, e.g. the sodium or calcium salt of lignosulfonic acid, of dodecylsulfate of of a mixture of fatty alcohol sulfates obtained from natural fatty acids. These compounds also comprise the salts of sulfated and sulfonated fatty alcohol/ethylene oxide adducts. The sulfonated benzimidazole derivatives preferably contain 2 sulfonic acid groups and one fatty acid radical containing 8 to 22 carbon atoms. Examples of alkylarylsulfonates are the sodium, calcium or triethanolamine salts of dodecylbenzenesulfonic acid, dibutylnaphthalenesulfonic acid, or of a condensate of naphthalenesulfonic acid and formaldehyde.

Also suitable are corresponding phosphates, e.g. salts of the phosphoric acid ester of an adduct of p-nonylphenol with 4 to 14 moles of ethylene oxide.

Non-ionic surfactants are preferably polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, saturated or unsaturated fatty acids and alkylphenols, said derivatives containing 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon moiety and 6 to 18 carbon atoms in the alkyl moiety of the alkylphenols.

Further suitable non-ionic surfactants are the water-soluble adducts of polyethylene oxide with polypropylene glycol, ethylenediaminopolypropylene glycol and alkylpolypropylene glycol containing 1 to 10 carbon atoms in the alkyl chain, which adducts contain 20 to 250 ethylene glycol ether groups and 10 to 100 propylene glycol ether groups. These compounds usually contain 1 to 5 ethylene glycol units per propylene glycol unit.

Representative examples of non-ionic surfactants are nonylphenolpolyethoxyethanols, castor oil polyglycol ethers, polypropylene/polyethylene oxide adducts, tributyl-phenoxypolyethoxyethanol, polyethylene glycol and octylphenoxypolyethoxyethanol.

Fatty acid esters of polyoxyethylene sorbitan, e.g. polyoxyethylene sorbitan trioleate, are also suitable non-ionic surfactants.

Cationic surfactants are preferably quaternary ammonium salts which contain, as N-substituent, at least one C_8-C_{22}alkyl radical and, as further substituents, unsubstituted or halogenated lower alkyl, benzyl or hydroxy-lower alkyl radicals. The salts are preferably in the form of halides, methylsulfates or ethylsulfates, e.g. stearyltrimethylammonium chloride or benzyldi(2-chloroethyl)ethylammonium bromide.

The surfactants customarily employed in the art of formulation are described, inter alia, in the following publications:

"1985 International Mc Cutcheon's Emulsifiers & Detergents", Glen Rock NJ USA, 1985,

M. and J. Ash, "Encyclopedia of Surfactants", Vol. I-III, Chemical Publishing Co., New York, 1980.

The agrochemical compositions usually contain 0.1 to 99 %, preferably 0.1 to 95 %, of the mixture according to the invention and 1 to 99.9 % especially 99.8 to 5 % of solid or liquid adjuvants, whereof 0 to 25 %, preferably 0.1 to 25 %, of a surfactant. While commercial ware is rather in the form of concentrates the end user prefers as a rule diluted compositions.

The compositions can also contain further additives, like stabilizers, anti-foaming agents, regulators of viscosity, binding agents, adhesifs as well as fertilizers and/or different active agent in order to achieve specific effects.

Agrochemical compositions of this kind are also a part of the present invention.

Active compounds or compositions with different biocidal properties can also be admixed to the compositions of this invention. Thus the new composition can contain besides the

compounds of the formula I and of the formulae II to IX e.g. also insecticides, fungicides, bactericides, fungistatics, bacteriostatics or nematocides.

The compositions according to the invention can generally be formulated, in detail, in accordance with the following Examples:

Formulation Examples

Example F1:

Formulation Examples for synergistic active ingredient mixtures of the formulae I and II, III, IV, V, VI, VII, VIII or IX (throughout, percentages are by weight)

a) Wettable powders	a)	b)	c)
compound I and one of the compounds II to IX	25 %	50 %	75 %
sodium lignosulfonate	5 %	5 %	- %
sodium lauryl sulfate	3 %	-	5 %
sodium diisobutylnaphthalenesulfonate	-	6 %	10 %
octylphenol polyethylene glycol ether (7-8 moles of ethylene oxide)	-	2 %	-
highly dispersed silicic acid	5 %	10 %	10 %
kaolin	62 %	27 %	-

The active ingredient mixture is thoroughly mixed with the adjuvants and the mixture is thoroughly ground in a suitable mill, affording wettable powders which can be diluted with water to give suspensions of the desired concentration.

b) Emulsifiable concentrate

compound I and one of the compounds II to IX	10 %
octylphenol polyethylene glycol ether (4-5 moles of ethylene oxide)	3 %
calcium dodecylbenzenesulfonate	3 %
castor oil polyglycol ether (36 moles of ethylene oxide)	4 %
cyclohexanone	30 %
xylene mixture	50 %

Emulsion of any required concentration can be obtained from this concentrate by dilution with water.

c) Dusts	a)	b)
compound I and one of the compounds II to IX	5 %	8 %
talcum	95 %	-
kaolin	-	92 %

Ready-for-use dusts are obtained by mixing the active ingredient mixture with the carrier and grinding the mixture in a suitable mill.

d) Extruder granulate

compound I and one of the compound II to IX	10 %
sodium lignosulfonate	2 %
carboxymethylcellulose	1 %
kaolin	87 %

The active ingredient mixture is mixed and ground with the adjuvants, and the mixture is subsequently moistened with water. The mixture is extruded and then dried in a stream of air.

e) Coated granulate

compound I and one of the compound II to IX	3 %
polyethylene glycol (mol. wt. 200)	3 %
kaolin	94 %

The finely ground active ingredient mixture is uniformly applied, in a mixer, to the kaolin moistened with polyethylene glycol. Non-dusty coated granulates are obtained in this manner.

f) Suspension concentrate

compound I and one of the compound II to IX	40 %
polyethylene glycol	10 %
nonylphenol polyethylene glycol ether (15 moles of ethylene oxide)	6 %
sodium lignosulfonate	10 %
carboxymethylcellulose	1 %
silicone oil in the form of a 75 % aqueous emulsion	1 %
water	32 %

The finely ground active ingredient mixture is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired concentration can be obtained by dilution with water.

Often it is more convenient to formulate the active substance of the formula I as well as the mixing partner of formulae II to IX individually, in order to mix them in the desired proportions shortly before the treatment in the applicator and to combine them with water as "tank mix".

A synergistic effect is always present in the case of herbicides, when the herbicidal action of the combination of compounds I and II, III, IV, V, VI, VII, VIII or IX is greater than the expected action of the active ingredients applied individually, when calculated according to "Colby".

The expected herbicidal action Ae for a given combination of two compounds can be calculated as follows (cf. COLBY, S.R., "Calculating synergistic and antagonistic response of herbicide combinations", Weeds 15, pages 20-22, 1967):

$$Ae = X + \frac{Y \cdot (100-X)}{100}$$

in which:

X = percentage inhibition of growth in the case of treatment with a herbicide I at a rate of application of p kg per hectare in comparison with the untreated control (= 0 %)

Y = percentage inhibition of growth in the case of treatment with a herbicide II, III, IV, V, VI, VII, VIII or IX at a rate of application of q kg per hectare in comparison with the untreated control

Ae = expected herbicidal action (percentage inhibition of growth in comparison with the untreated control) after treatment with herbicide mixture I and II, III, IV, V, VI, VII, VIII or IX at a rate of application of p + q kg active ingredient per hectare.

If the action actually observed is greater than the expected value Ae then synergism has been achieved.

The synergistic effect of the combinations of compounds I and II, III, IV, V, VI, VII, VIII or IX is demonstrated in the following Examples.

Biological Examples

Example 1: Growth inhibition of cereal

Summer barley of the type "Iban" is sown in plastic beakers of 15 cm diameter filled with sterilized soil and raised in a climatized room at a day temperature of 10 to 15°C and a night temperature of 5 to 10°C. The light period was 13.5 hours daily at an intensity of about 25000 Lux.

Abour 34 days after sowing and thinning out to 4 plants per pot, the active substance or mixture was sprayed as an aqueous broth in the application rate given in the table of results. The amount of water used corresponds to about 500 l/ha. After the application, the plants are kept in the greenhouse at a day temperature of at least 10°C. The light period was at least 13.5 hours daily.

The evaluation takes place 14 to 35 days after the treatment (the duration is given in the tables). The activity is measured and expressed in percent of the new growth, compared to not treated tables (plants is meant). 0 % stands for no inhibitory action (same growth as with not treated plants), 100 % means complete growth stop. The height of the new growth is represented in % of the average of that of not treated control plants.

The results of growth inhibition are summarized in the following table 1. The combinations according to this invention that were tested show a clear synergistic increase in activity.

Table 1:

Compund/application rate g/ha		Time of evaluation Days after application	% growth inhibition	
I	IIa	34 days	measured	expected (calculated according to Colby)
250	-		12	-
500	-		20	-
-	1000		0	-
-	2000		0	-
250 +	1000		57	12
250 +	2000		59	12
500 +	1000		71	20
500 +	2000		69	20
I	IIb	34 days		
250	-		12	-
500	-		26	-
-	1000		8	-
-	2000		12	-
250 +	1000		82	19
250 +	2000		86	23
500 +	1000		91	32
500 +	2000		91	35
I	IIc	34 days		
250	-		12	-
500	-		26	-
-	500		10	-
-	1000		12	-
250 +	500		35	21
250 +	1000		42	23
500 +	500		60	33
500 +	1000		64	35
I	IIIa	35 days		
250	-		8	-
500	-		23	-
-	1000		2	-
-	2000		2	-
250 +	1000		17	10
250 +	2000		29	10
500 +	1000		32	25
500 +	2000		46	25

Table 1 (continuation):

Compund/application rate g/ha		Time of evaluation Days after application	% growth inhibition	
I	IIId	32 days	measured	expected (calculated according to Colby)
125	-		3	-
250	-		8	-
-	250		7	-
-	500		12	-
-	1000		12	-
125 +	250		30	10
125 +	500		48	14
125 +	1000		53	23
250 +	250		41	14
250 +	250		58	19
250 +	250		69	28
I	IVa	35 days		
250	-		12	-
500	-		23	-
-	1000		0	-
-	2000		0	-
250 +	1000		27	12
250 +	2000		31	12
500 +	1000		27	23
500 +	2000		60	23
I	IVc	19 days		
250	-		8	-
500	-		23	-
-	1500		2	-
-	3000		2	-
250 +	1500		38	10
250 +	3000		49	10
500 +	1500		47	25
500 +	3000		74	25
I	V	35 days		
250	-		8	-
500	-		23	-
-	500		8	-
-	1000		12	-
250 +	500		36	15
250 +	1000		66	19
500 +	500		61	29
500 +	1000		68	32

Table 1 (continuation):

Compound/application rate g/ha		Time of evaluation Days after application	% growth inhibition	
I	VIa	35 days	measured	expected (calculated according to Colby)
250	-		8	-
500	-		23	-
-	1000		8	-
-	2000		10	-
250 +	1000		27	15
250 +	2000		41	17
500 +	1000		47	29
500 +	2000		48	31
I	VIb	35 days		
250	-		8	-
500	-		23	-
-	1000		8	-
-	2000		6	-
250 +	1000		29	15
250 +	2000		32	14
500 +	1000		38	29
500 +	2000		55	28
I	VII	34 days		
250	-		5	-
500	-		12	-
-	500		1	-
-	1000		3	-
250 +	500		15	6
250 +	1000		19	8
500 +	500		30	13
500 +	1000		49	13
I	VIII	35 days		
125	-		3	-
250	-		8	-
-	60		8	-
-	125		14	-
- +	250		41	-
125 +	60		36	11
125 +	125		40	17
125 +	250		70	43
250 +	60		53	15
250 +	125		75	21
250 +	250		84	46

Example 2: Growth inhibition of grasses

A mixture of the grasses Poa, Festuca, Lolium, Bromus and Cynodon is sown into plastic dishes of 15 cm diameter that were filled with sterile soil and raised in the greenhouse at a day temperature of 21°C and a night temperature of 17°C. The light period is 13.5 hours per day at a light intensity of minimum 7000 Lux.

After emerging the grasses were cut back every week to about 6 cm height. About 42 days after sowing and 1 day after the last cut, the grass was treated with the amount of active substance or combination of active substances in the application rate in g/ha given in the tables of results, in the form of an aqueous broth. The amount of water used was about 500 l/ha. The test was evaluated 20 days after the treatment. The height of the new growth was measured and is expressed as % inhibition as compared to the average of the new growth of the not treated control plants.

The results of growth inhibition of grasses are summarized in the following table 2. The mixtures tested show a clearly synergistic activity.

Table 2:

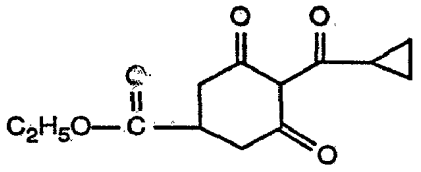
Compound/application rate g/ha			Time of evaluation Days after application	% growth inhibition	
I		IIa	20 days	measured	expected (calculated according to Colby)
250		-		15	-
500		-		33	-
-		1500		4	-
-		3000		8	-
250	+	1500		38	18
250	+	3000		38	22
500	+	1500		49	36
500	+	3000		49	38
I		IIId	20 days		
250		-		15	-
500		-		33	-
-		1000		35	-
-		2000		60	-
250	+	1000		66	45
250	+	2000		86	66
500	+	1000		79	56
500	+	2000		83	73
I		VIa	20 days		
250		-		11	-
500		-		31	-
-		1000		18	-
-		2000		21	-
250	+	1000		49	27
250	+	2000		52	30
500	+	1000		55	43
500	+	2000		59	45

Table 2: (continuation)

Compound/application rate g/ha		Time of evaluation Days after application	% growth inhibition	
I	VIb	20 days	measured	expected (calculated according to Colby)
250	-		11	-
500	-		31	-
-	1000		1	-
-	2000		8	-
250 +	1000		35	12
250 +	2000		37	18
500 +	1000		52	32
500 +	2000		52	37
I	VII	20 days		
500	-		39	-
1000	-		46	-
-	500		9	-
-	1000		9	-
-	2000		13	-
500+	500		56	44
500+	1000		65	44
500+	2000		73	47
1000+	500		79	44
1000+	1000		81	51
1000+	2000		87	53
I	IX	20 days		
500	-		33	-
750	-		52	-
-	5		0	-
-	15		55	-
500 +	5		48	33
500 +	15		91	70
750 +	5		76	52
750 +	15		97	78

~~Patent claims~~ The claims defining the invention are as follows:

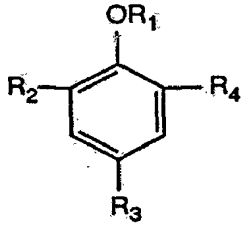
1. A synergistically acting composition for regulating plant growth, which is characterized that it contains besides inert carriers, auxiliaries and adjuvants, as active component 4-cyclopropionyl-3,5-cyclohexanedione-1-carboxylic acid of formula I



(I)

besides a synergistically active amount of a further active compound selected from among

a) phenolethers of the formula II



(II)

wherein

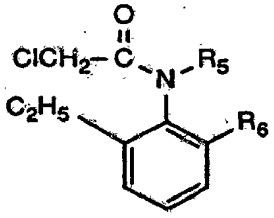
R_1 is an acid or the C_1-C_4alkyl ester of a radical $-CH_2COOH$, $-CH(CH_3)COOH$, $-(CH_2)_3COOH$ or the nitrobenzoic-5-yl radical,

R_2 is chlorine or methyl,

R_3 is chlorine and

R_4 is hydrogen, chlorine or methyl; or

b) chloracetanilides of the formula III



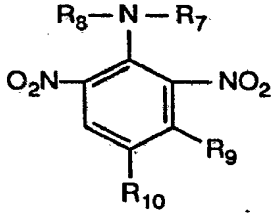
(III)

wherein

R_5 is methyl or ethyl and

R_6 is methoxymethyl, ethoxymethyl or 2-methoxy-1-methylethyl; or

c) dinitroanilines of the formula IV



(IV)

wherein

R_7 is hydrogen or C_1-C_4alkyl,

R_8 is C_1-C_4alkyl, benzyl or halobenzyl,

R_9 is hydrogen or halogen and

R_{10} is methyl, trihalomethyl or chlorine; or

d) N-benzoyl-N-(3,4-dichlorophenyl)-DL-alanine acid ethyl ester; or

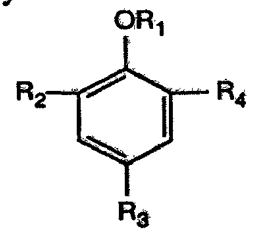
e) a quaternary ammonium salt selected from among 1,1-dimethylpiperidine chloride and 2-chloro-N,N,N-trimethylethylammonium chloride; or

f) 2-chloroethylphosphonic acid; or

g) 1-phenyl-4,4-dimethyl-2(1H-1,2,4-triazol-1-yl)-pent-1-en-3 -ol; or

h) 5-(1-methylthioxycyclopropane-1-yl)-2-(trans-3-chloroallylo ximino)-propionyl-cyclohexane-1,3-dione.

2. A composition for regulating plant growth according to claim 1, which is characterized that it contains, besides inert adjuvants and the active compound of formula I, a synergistically active amount of a phenol ether of formula II



(II)

wherein

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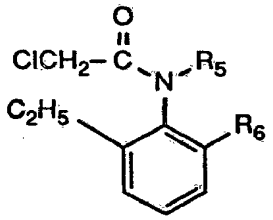
R_1 is an acid or the C_1-C_4alkyl ester of a radical -CH_2COOH, -$CH(CH_3)COOH$, -$(CH_2)_3COOH$ or the nitrobenzoic-5-yl radical,
R_2 is chlorine or methyl,
R_3 is chlorine and
R_4 is hydrogen, chlorine or methyl, or in the proportion active compound of formula I to active compound of formula II of 10:1 to 1:10.

3. A composition for regulating plant growth according to claim 1, which is characterized that it contains a synergistically active amount of a compound selected from among 2-nitro-5-(2,4-dichlorophenoxy)-benzoic acid, 2-(4-chloro-2-methyl-phenoxy-)-propionic-acid, 2-(2,4-dichlorophenoxy)acetic-acid, 2-(4-chloro-2-methyl-phenoxy)-~~essigsäure und~~ acetic acid and 4-(4-chloro-2-methylphenoxy)-butyric-acid.

4. A composition for regulating plant growth according to claim 1, which is characterized that it contains besides inert adjuvants and the active compound of formula I, a synergistically active amount of a chloro acetanilide of the formula III



(III)

wherein
R_5 is methyl or ethyl and
R_6 is methoxymethyl, ethoxymethyl or 2-methoxy-1-methylethyl, in the proportion of active compound of the formula I to active compound of the formula III of 10:1 to 1:10.

5. A composition for regulating plant growth according to claim 1, which is characterized, that it contains a synergistically active amount of a compound selected from among 2-chloro-2'-ethyl-6'-methyl-N-(2-methoxy-1-methylethyl)acetanilide, 2-chloro-2',6'-diethyl-N-methoxymethylacetanilide, 2'-chloro-N-ethoxymethyl-6'-ethylacet-o-toluidide and 2-chloro-N-(methoxycarbonylaminomethyl)-2',6'-diethylacetanilide.

6. A composition for regulating plant growth according to claim 1, which is characterized that it contains, besides inert adjuvants and the active compound of formula I, a synergistically active amount of a 2,6-dinitroanilide of the formula IV

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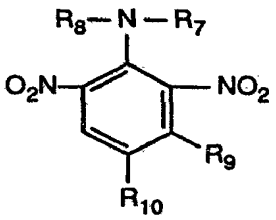


(IV)

wherein

R_7 is hydrogen or C_1-C_4alkyl,

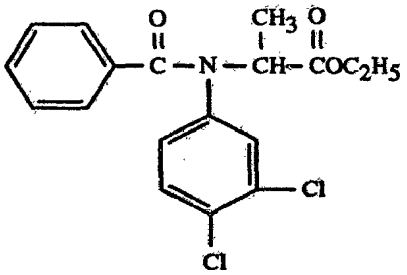
R_8 is C_1-C_4alkyl, benzyl or halobenzyl,

R_9 is hydrogen or halogen and

R_{10} is methyl, trihalomethyl or chlorine, in the proportion of active compound of the formula I to active compound of the formula IV of 10:1 to 1:10.

7. A composition for regulating plant growth according to claim 1, which is characterized that it contains a synergistically active amount of a compound selected from among N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitroaniline, N-ethyl-N-(2'-chloro-6'-fluorobenzyl)-2,6-dinitro4-trifluoromethylaniline and N_1,N_1-diethyl-2,6-dinitro-4-trifluoro-methyl-1,3-phenyldiamine.

8. A composition for regulating plant growth,which is characterized that it contains besides inert adjuvants and the active compound of formula I, a synergistically active amount of the ethyl ester of N-benzoyl-N-3,4-dichlorophenyl)-DL-alanine of the formula V



(V)

in the proportion active compound of formula I to active compound of formula V of 10:1 to 1:10.

9. A composition for regulating plant growth according to claim 1, which is characterized that it contains besides inert adjuvants and the active compound of formula I, a syner-

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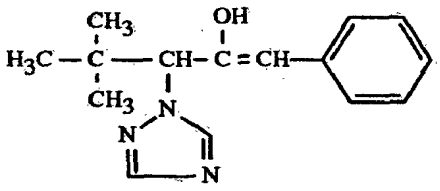
gistically active amount of a quaternary ammonium salt, which is selected from among 1,1-dimethylpiperidine chloride and 2-chloroethyl-N,N,N-trimethylammoniumchloride, in the proportion of active compound of the formula I to ammonium salt of 10:1 to 1:10.

10. A composition for regulating plant growth according to claim 1 which is characterized that it contains besides inert adjuvants and the active compound of formula I, a synergistically active amount of 2-chloroethylphosphonic acid, in the proportion of active compound of the formula I to 2-chloroethylphosphonic acid of 10:1 to 1:10.

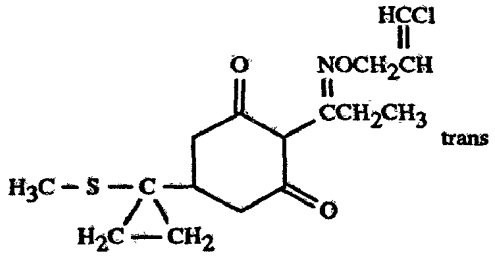
11. A composition for regulating plant growth, which is characterized that it contains besides inert adjuvants and the active compound of formula I, a synergistically active amount of 1-phenyl-4,4-dimethyl-2-(1H-1,2,4-triazol-1-yl)pent-1-en-3-ol , of the formula VIII



(VIII),

in the proportions of active compound of the formula I to compound of the formula VIII of 10:1 to 1:10.

12. A composition for regulating plant growth, which is characterized that it contains besides inert adjuvants and the active compound of formula I, a synergistically active amount of 5-(1-methylthiocyclopropane-1-yl)-2-[1-(trans-3-chloroallyloximino)-propionyl]-cyclohexane-1,3-dione of the formula IX



(IX)

in the proportion of active compound of the formula I to active compound of the

formula IX of 100:1 to 1:10.

13. A composition for regulating plant growth according to claim 1, which is characterized that it contains besides 99.9 to 5% solid or liquid inert adjuvants, among them 0.1 to 25% of a surfactant, 0.1 to 95% of a combination of active compounds of the compound of formula I with a compound of one of the formulae II to IX in the proposition of 100:1 to 1:10.

14. A synergistically acting composition for regulating plant growth, substantially as hereinbefore described with reference to any one of Formulation Examples F1(a) to (f).

15. A method of regulating plant growth, which is characterized in that one applies to the plants or their locus an active amount of a composition according to any one of claims 1 to 14, respectively a tank mix containing the active compound of the formula I and a mixing partner of formulae II to IX.

16. A method of inhibiting plant growth in field cultures of useful plants and grasses which is characterized in that one applies to the plants post-emergently an active amount of a composition according to any one of claims 1 to 14.

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